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NORMAL COORDINATE ANALYSIS OF CRYSTALS

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PROGRAM SUMMARY

Title of program: NORMAL COORDINATE ANALYSIS

Catalogue number: ACKJ

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Computer: CYBER 74; *Installation*: State University Groningen

Operating system: SCOPE 3.4.1., level 373

Program language used: FORTRAN 4.1.

High speed store required: 155k (octal)

No. of bits in a word: 60

Overlay structure: None

No. of magnetic tapes required: None

Other peripherals used: Card reader, line printer

Number of cards in combined program and test deck: 1325

Card punching code: IBM(029) EBCDIC

Keywords: Solid state, dynamical matrix, normal coordinate analysis, infrared spectra analysis, eigenvalue problem, threshold Jacobi method, Householder procedure.

Nature of the physical problem
A program has been written for solving the vibrational secular equation in cartesian coordinates [1] and for adjusting a set of force constants to give a fit of calculated and observed frequencies [2] which are measured by means of infrared transmission spectroscopy.

Method of solution
Two methods for calculating the eigenvalues and eigenvectors are included in the program deck. These methods are: the threshold serial Jacobi method [3] and the Householder procedure [4]. Although the latter is faster than the Jacobi method, the eigenvectors are more accurate in the case of the threshold serial Jacobi procedure.

Restriction on the complexity of the problem
The program is dimensioned for 20 atoms per unit cell. The number of degrees of freedom may be increased to 99, depending on the available storage capacity.

Typical running time
For the eigenvalue problem solved by threshold serial Jacobi method for $KNiF_3$ (without iteration procedure): 12.6 sec.

Unusual features of the program
Using the symmetry coordinates, it is possible to diagonalize the dynamical matrix in blocks. The symmetry coordinates can be calculated in some cases by the method and the program given by Warren and Worlton [5], using a reducible multiplier representation of the point group of the wavevector ($\boldsymbol{k} = \mathbf{0}$). However, the input of the symmetry coordinates is not necessary for our program. Block-diagonalization of the dynamical matrix set up in cartesian coordinates is often not very useful for solving the eigenvalue problem.

References
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LONG WRITE-UP

1. Introduction

A phenomenon of great interest is the existence of vibrational excitation modes in crystals. These lattice vibrations contribute to the specific heat of crystals and are important because of their interaction with electrons which contribute to the electrical resistivity. Many investigations have been carried out in order to obtain an insight into the nature of the interatomic forces in crystals by determining infrared and Raman spectra. It is clear that due to the large interest of physicists and physical chemists in this field there exists a great deal of overlap in computer programs.

Schachtschneider [1] has written several programs for solving the vibrational secular equation and in addition programs for the least-squares refinement of force constants in the case of polyatomic molecules. The purpose of the present paper is to introduce a computer program which solves the vibrational secular equation for crystals by means of procedures which are faster and involve a different method for adjusting a set of force constants fitting calculated frequencies to observed frequencies.

The program is written for the analysis of infrared spectra of crystals. When $\boldsymbol{k} = 0$, the crystal has all the symmetry of the translation group. The atoms move either in phase or out of phase. The former motion is the acoustical vibration which has a frequency of zero. The structure of the program corresponds to that of the programs of Mikawa [2] and Schachtschneider. In all known programs in this field, the program MIHDI3 (Share distribution no. 705 and no. 731), written by Corbato of the MIT-computation centre, is used for diagonalizing a real symmetric matrix by means of the classical Jacobi method. The original program was coded in SAP for the IBM-704 and was modified to FORTRAN-II by Merven, also of MIT, and to FORTRAN-IV by Schachtschneider et al. However, this program is not very fast. A subroutine has been written by which the computer time for the eigenvalue problem is reduced by about 30–40%. It is obviously important to use a fast subroutine for solving the vibrational secular equation during the refinement of many force constants. We include in the program an option for solving the secular equation by Householder's procedure [3]. Although the Jacobi method has the advantage of giving eigenvectors which are orthogonal, the faster Householder method may in some cases be preferable. According to Wilkinson [4] this failing of Householder's method is not such as to justify the use of the Jacobi method, which is slower.

In the following section, we give an outline of the necessary theoretical background for the calculation. In section 3, we describe the program organization as well as a comparison between the methods for solving the vibrational secular equation.

2. Theory

The dynamical matrix formulation of the vibrational motions of a lattice leads to the normal frequencies and normal coordinates in the same way as Wilson's treatment for free molecules [5]. The derivation of this dynamical matrix by means of Wilson's "FG"-method has been given by Piseri and Zerbi [6]. Shimanouchi et al. [7] have observed very properly that the cartesian coordinate method is more convenient for a normal vibration calculation in crystals than the internal coordinate method.

The optically active cartesian and internal coordinate vectors are given by, respectively

$$\boldsymbol{X}_{\mathrm{op}}(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_n \boldsymbol{x}_n \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}(n)}, \tag{1}$$

$$\boldsymbol{R}_{\mathrm{op}}(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_n \boldsymbol{r}_n \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}(n)}, \tag{2}$$

where N is the number of unit cells, $\boldsymbol{x}_n$ the matrix of cartesian displacements coordinates and $\boldsymbol{r}_n$ the matrix of internal displacements coordinates. The internal and cartesian phonon coordinate systems are related by the transformation matrix, $\boldsymbol{B}$:

$$\boldsymbol{R}_{\mathrm{op}}(\boldsymbol{k}) = \sum_n \boldsymbol{B}_n \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}(n)} \boldsymbol{X}_{\mathrm{op}}(\boldsymbol{k}), \tag{3}$$

or

$$\boldsymbol{R}_{\mathrm{op}} = \boldsymbol{B}_{\mathrm{op}} \boldsymbol{X}_{\mathrm{op}}. \tag{4}$$

The kinetic energy T is given by

$$2T = \dot{\boldsymbol{X}}^{\mathrm{t}}_{\mathrm{op}} \boldsymbol{M} \dot{\boldsymbol{X}}_{\mathrm{op}}. \tag{5}$$

The vibrational potential energy is expanded into a Taylor series of the displacements coordinates x_n. Neglecting higher order terms, the potential energies can be written for small amplitudes of vibration, assuming the Born–Oppenheimer theorem [8], in matrix notation as

$$2V = \boldsymbol{R}^{\mathrm{t}}_{\mathrm{op}} \boldsymbol{F}_{\mathrm{op}}(R) \boldsymbol{R}_{\mathrm{op}} \tag{6}$$

in which $\boldsymbol{F}_{\mathrm{op}}(R)$ is a symmetric matrix which gives the potential energy in terms of internal valence coordinates R. We describe the elements of the force constant matrix $\boldsymbol{F}_{\mathrm{op}}(R)$ as a linear function of the independent parameter force constants $\boldsymbol{\Phi}_l$:

$$F_{\mathrm{op}\,ik} = \sum_l Z_{ikl} \boldsymbol{\Phi}_l. \tag{7}$$

The mass-adjusted cartesian symmetry coordinate vector is given by

$$\boldsymbol{S}^{\mathrm{c}}_{\mathrm{op,m}} = \boldsymbol{U}_x \boldsymbol{M}^{-1/2} \boldsymbol{X}_{\mathrm{op}} = \boldsymbol{U}_{x,\mathrm{m}} \boldsymbol{X}_{\mathrm{op}}, \tag{8}$$

where $\boldsymbol{U}_x$ is the orthogonal symmetry matrix based on group-theoretical considerations. A general rule for the construction of symmetry coordinates can be written as

$$S^{\gamma}_j = N \sum_R \chi^{\gamma}_R (RS_i), \tag{9}$$

where RS_i represents the coordinate after the operator has acted on the internal coordinate S_i. The summation is taken over the operators in the factor group, isomorphic with the point group. χ^{γ}_R represents the character χ of the irreducible representation γ with the operator R.

The internal coordinate vector $\boldsymbol{R}_{\mathrm{op}}$ can be written by means of eqs. (4) and (8) as

$$\boldsymbol{R}_{\mathrm{op}} = \boldsymbol{B}_{\mathrm{op}} \boldsymbol{U}^{\mathrm{t}}_{x,\mathrm{m}} \boldsymbol{S}^{\mathrm{c}}_{\mathrm{op,m}}. \tag{10}$$

The kinetic energy is given by

$$2T = \dot{\boldsymbol{S}}^{\mathrm{c}^{\mathrm{t}}}_{\mathrm{op,m}} \dot{\boldsymbol{S}}^{\mathrm{c}}_{\mathrm{op,m}}, \tag{11}$$

and the potential energy by

$$2V = \boldsymbol{S}^{\mathrm{c}^{\mathrm{t}}}_{\mathrm{op,m}} \boldsymbol{U}_{x,\mathrm{m}} \boldsymbol{B}^{\mathrm{t}}_{\mathrm{op}} \boldsymbol{F}_{\mathrm{op}}(R) \boldsymbol{B}_{\mathrm{op}} \boldsymbol{U}^{\mathrm{t}}_{x,\mathrm{m}} \boldsymbol{S}^{\mathrm{c}}_{\mathrm{op,m}}. \tag{12}$$

The Lagrange equations of motion lead then to the secular determinant in which $\boldsymbol{\Lambda}$ represents the eigenvalue matrix:

$$\det|\boldsymbol{F}^{\mathrm{c}}_{\mathrm{s,op,m}} - \boldsymbol{E}\boldsymbol{\Lambda}| = 0, \tag{13}$$

where

$$\boldsymbol{F}^{\mathrm{c}}_{\mathrm{s,op,m}} = \boldsymbol{U}_{x,\mathrm{m}} \boldsymbol{B}^{\mathrm{t}}_{\mathrm{op}} \boldsymbol{F}_{\mathrm{op}}(R) \boldsymbol{B}_{\mathrm{op}} \boldsymbol{U}^{\mathrm{t}}_{x,\mathrm{m}}. \tag{14}$$

Block diagonalization of the dynamical matrix, set up in cartesian coordinates by means of the matrix $\boldsymbol{U}_{x,\mathrm{m}}$ is often not very useful for solving the eigenvalue problem. Only in the case of triply degenerated vibrations is it useful. If non-degenerate or doubly degenerate vibrations are involved, all cartesian directions must be included in the eigenvalue problem.

The eigenvectors of eq. (13) are the mass-adjusted cartesian displacements $\boldsymbol{L}^{\mathrm{c}}_{\mathrm{m}}$. By means of the transformation matrix $\boldsymbol{U}^{\mathrm{t}}_{x,\mathrm{m}}$, cartesian displacements can be calculated as

$$\boldsymbol{L}^{\mathrm{c}} = \boldsymbol{U}^{\mathrm{t}}_{x,\mathrm{m}} \boldsymbol{L}^{\mathrm{c}}_{\mathrm{m}}. \tag{15}$$

Several methods for adjusting the force constants are known. Procedures are developed by Mann et al. [9]. Schachtschneider programmed the method of King [10]. We used the method given by Shimanouchi and Suzuki [11]. The procedure of Shimanouchi and Suzuki is based on the mathematical theory of minimization of functions [12,13]. In the method of adjusting we used the eigenvectors of a previous solution in the next eigenvalue calculation. If $\Delta\boldsymbol{F}$ constitutes a small correction, the matrix $\boldsymbol{P}$ is nearly diagonal (we omit now the indices c, s, op and m):

$$\boldsymbol{P} = \boldsymbol{L}_0^{-1} (\boldsymbol{F}_0 + \Delta\boldsymbol{F}) \boldsymbol{L}_0 = \boldsymbol{\Lambda}_0 + \boldsymbol{L}_0^{-1} \Delta\boldsymbol{F} \boldsymbol{L}_0, \tag{16}$$

in which $\boldsymbol{L}_0$ are the eigenvectors in the first cycle. The correction $\boldsymbol{L}_0^{-1} \Delta\boldsymbol{F} \boldsymbol{L}_0$ is connected with the deviation in observed eigenvalues and calculated eigenvalues, which is written as $\Delta\boldsymbol{\Lambda}$, as follows

$$\boldsymbol{L}_0^{-1} \Delta\boldsymbol{F} \boldsymbol{L}_0 \approx \Delta\boldsymbol{\Lambda}. \tag{17}$$

The coefficients of the elements of $\Delta\boldsymbol{F}$ are the elements of the jacobian $\boldsymbol{J}$ of $\boldsymbol{\Lambda}$ with respect to $\Delta\boldsymbol{F}$:

$$\boldsymbol{J}\,\Delta\boldsymbol{F} = \Delta\boldsymbol{\Lambda}. \tag{18}$$

The elements $J_{p,k}$ in the jacobian are now given by eq. (7):

$$J_{p,k} = \delta\lambda_p / \delta\phi_k = \boldsymbol{L}_p^{-1} \boldsymbol{Z}_k \boldsymbol{L}_p. \tag{19}$$

The elements of the potential energy distribution among the force constants $\boldsymbol{\Phi}$ can be calculated for each normal mode by the following procedure. The

potential energy V is given by:

$$2V = \sum_p \lambda_p Q_p^2, \tag{20}$$

where Q_p represents the normal coordinate of mode p. By eqs. (20) and (16) it follows for the potential energy for a unit displacement of the normal mode p:

$$\lambda_p = \sum_{i,j} L_{ip} L_{jp} F_{ij}. \tag{21}$$

The fractional contribution to λ_p of the elements of the $\boldsymbol{F}$-matrix is given by eq. (21) as

$$L_{ip}^2 F_{ii}/\lambda_p \tag{22}$$

for the diagonal terms in $\boldsymbol{F}$, and as

$$2L_{jp} L_{ip} F_{ij}/\lambda_p \tag{23}$$

for the off-diagonal elements where $i < j$.

3. Program

The program consists of a main program and eight subroutines: TRANSF, JACOBI, ORDEN, HOUSH1, HOUSH2, HOUSH3, HOUSH4, HOUSH5. All input cards are read in the main program. The main program contains the matrix multiplications of section 2.

3.1. Subroutine TRANSF

Subroutine TRANSF calculates the matrix $\boldsymbol{F}^{c}_{s,op,m}$ [eq. (13)].

3.2. Subroutine JACOBI

The subroutine JACOBI computes the eigenvalues and, if wanted, the eigenvectors of the real symmetrical matrix $\boldsymbol{F}^{c}_{s,op,m}(n \times n)$. The method used is the threshold serial Jacobi method. This procedure avoids the inefficient rotations occurring in the original Jacobi method [14]. In the case of the original Jacobi procedure, Goldstine and Horwitz [15] demonstrated the convergence of the procedure if the pair (i, j) is chosen so that the sum of the squares of the absolute values of the off-diagonal elements (i, j) and (j, i) is largest. Loizou [16] proved the quadratic convergence of this method if convergence has taken place to a certain extent.

Searching for the largest off-diagonal element is time absorbing. It requires about $\frac{1}{2}n^2$ subtractions. The simplest scheme avoiding these subtractions is to run along the elements sequentially and thereafter to return to the first element. A variant of this, called the serial Jacobi method, is based on the choice of a threshold value. Only those elements (i, j) are transformed if the absolute value of the element is higher than this threshold. The threshold is reduced if all off-diagonal terms are lower than the threshold. The procedure is repeated until all the off-diagonal elements are below the lowest threshold. Using a well-chosen threshold, this "threshold serial Jacobi process" is faster than the original Jacobi procedure. The total computation time for calculating the eigenvalues by means of the classical Jacobi process is about $12n^3M$; where M stands for the computer time necessary for one multiplication. In the case of the threshold serial Jacobi procedure the off-diagonal elements do not differ significantly from zero after n^2 to $2n^2$ rotations. The total computer time is about $4n^3M$ to $8n^3M$. For the error-analysis of this threshold serial Jacobi method, see ref. [4], p. 279.

3.3. Subroutine ORDEN

The eigenvalues are delivered in an arbitrary order by the subroutine JACOBI. These eigenvalues and eigenvectors have to be used in the fitting procedure together with the observed frequencies. Therefore, the subroutine ORDEN rearranges the eigenvalues and eigenvectors in decreasing or increasing order.

3.4. Subroutine HOUSH1, HOUSH2, HOUSH3, HOUSH4, HOUSH5

This set of subroutines computes the eigenvectors and eigenvalues of the real symmetrical matrix $\boldsymbol{F}^{c}_{op,s,m}$. The method of calculation is the Householder method. We have included in the structure of the program the possibility of calculating the eigenvectors and eigenvalues by means of the Householder method, because of its rapidity. The method of Householder reduces a matrix $\boldsymbol{A}$ to the tridiagonal form $\boldsymbol{B}$, using the elementary hermitian orthogonal transformations. The calculation time for this reduction is about $2n^3M$, while the calculation of the eigenvalues absorbs about n^2M computation time. Furthermore,

the storage option inherent to the Householder procedure is more effective than in the case of the Jacobi method. However, if orthogonal eigenvectors are wanted, even with (almost) coincident eigenvalues, the Jacobi method is safer, but it consumes more computer time and storage capacity if the dimensions are large ($n \gg 15$).

In our case we need the eigenvectors of a previous solution in the fitting procedure [see eq. (16)]. For a quick normal-coordinate analysis one can start using the method of Householder for adjusting the force constants to fit the calculated frequencies to the observed frequencies until a certain variance is reached; thereafter the fitting procedure can be continued with the Jacobi method which then gives the eigenvectors as well as the final values of the force constants. For the error analysis of this procedure see ref. [4], p. 297.

3.4.1. Subroutine HOUSH1

This subroutine contains only the calls for the other subroutines concerning the Householder procedure.

3.4.2. Subroutine HOUSH2

The symmetric matrix $\boldsymbol{A}$ is reduced to the tridiagonal for $\boldsymbol{B}$ using elementary symmetrical orthogonal transformations.

3.4.3. Subroutine HOUSH3

Subroutine HOUSH3 calculates the eigenvalues of the symmetrical tridiagonal matrix $\boldsymbol{B}$ by the method of bisection [17].

3.4.4. Subroutine HOUSH4

For a given eigenvalue of the symmetrical tridiagonal matrix $\boldsymbol{B}$, the eigenvector is calculated. The method is based on that usually known as inverse iteration or Wielandt iteration [18].

3.4.5. Subroutine HOUSH5

The eigenvectors of the tridiagonal matrix $\boldsymbol{B}$, calculated in HOUSH4, are transformed to the eigenvectors of the original symmetric matrix $\boldsymbol{A}$.

4. Input/output

The input cards are listed in table 1. The first card

Table 1

Card number	Parameter	Description of parameter	FORMAT
1.	IND	Start of the calculation of IND.GT.0	I3
2.	OPT	Logical, debugging printouts if OPT=.TRUE.	NAMELIST NAM1
	IFU	Logical, matrix U is read if IFU=.TRUE.	
	IFJ	Logical, eigenvalues are calculated with threshold serial Jacobi method if IFJ=.TRUE., else calculation by Householder method	
	IFP	Logical, weighted factors are read if IFP=.TRUE., else these are calculated	
	IFB	Logical, *B*-matrix is read from catalogued file if IFB=.TRUE., else from cards	
	PROBNO	Numbering of the problem	
	NOAT	Number of atoms	
	NOQ	Number of internal coordinates (= number of rows in *B*)	
	NOXS	Number of symmetry coordinates	
	NOF	Number of force constants	
	NOZ	Number of non-zero elements in *Z*-matrix	
	NOIT	Number of iterations	
3.	REC(I)	Two information cards	12A6
4.		IFU=.TRUE; *U*-matrix is read from cards:	
	NROW(K)	Row number	4(2I3,F12.6)
	NCOL(K)	Column number	
	DAT(K)	Value of *U*-element, last element should be NROW=−03	
5.	DAT(K)	Read atomic weights	6F12.6
6.		IFB=.TRUE. *B*-matrix is read from ITAPE, catalogued as sequential file, else from cards:	

Table 1 (continued)

	NROW(K)	Row number	4(2I3,F12.6)
	NCOL(K)	Column number	
	DAT(K)	Value of B-element, last element should be NROW=−05	
7.	DAT(K)	Column vector force constants	6F12.6
8.		Z-matrix	
	NROW(K)	Row number	4(3I3,F9.6)
	NCOL(K)	Column number	
	NF(K)	Number in force constant vector	
	DAT(K)	Value for valence force field or Urey–Bradley force field. Last element should be NROW =−02	
9.	DEL	Variation in force constants	3F12.6
	EPS	Covergence criterium	
	RHO	Reduction factor	
10.	DAT(K)	Observed frequencies	6F12.6
11.	DAT(K)	IFP=.TRUE., weighted factors are read, else these are calculated	6F12.6
12.	KRL(I)	Force constants number for variation during the iteration process; if NOIT is equal zero this card should be omitted	26I3
13.	IND	See card 1.; if IND.LT.0 the run is terminated and not a following problem is started	I3

is a control card for the continuation of the calculation for another problem. It is possible to calculate several problems. Because of its flexibility the NAMELIST facility is used. This is not ASA FORTRAN, but is available on most computer systems. Three or two matrices are read. It is not necessary to read the orthogonal symmetry matrix U_x. The matrix U_x can be found by means of the factor group analysis. The symmetry coordinates can be calculated in some cases by the method and program given by Worlton and Warren [19], using a reducible multiplier representation of the point group of the wavevector k=**0**. The matrix B can be set up easily because the elements of this matrix are essentially the direction cosines of the vectors r [5], the internal valence coordinates. Schachtschneider has written a program for constructing this B-matrix in the case of molecules [20]. The matrix Z is a rectangular matrix of dimensions $k \times l$, where k is the number of force constants in $F(R)$ and l is the number of parameters in Φ. The elements of Z are determined by the model. The element Z_{jkl} is equal to one in the test run. It is also possible that the Φ_k are a set of Urey–Bradley [21] force constants. The Urey–Bradley force field adds interaction terms to the simple valence force field. The elements Z_{jkl} are then not necessarily equal to one.

The form of the output is illustrated at the end of this paper. It is possible by putting the logical input variable (see table 1) OPT=.TRUE. to get debugging print-outs. The results of the matrix multiplications, given in section 2 are printed. If OPT=.FALSE. and the number of iterations (NOIT) is not equal to zero, only the changes in the standard deviation and force constants are printed during the refinement of the force field. The subscripts of the matrices are printed as given by the input cards (see table 1).

The eigenvectors, mass-adjusted L^c_m, and cartesian displacements L^c are printed so that the column refers to the eigenvalue and the row number to the cartesian coordinate $x_1y_1z_1 \ldots . x_ny_nz_n$ of the atoms. In the case of the jacobian matrix J, the column number is the number of the force constants and the row number is the number of the eigenvalue.

5. Description of the TEST RUN

As TEST RUN we have chosen an example known in the literature. Shimanouchi et al. [22] have given a very extended normal-coordinate analysis for the compounds with perovskite structure: $KNiF_3$, $KMgF_3$ and $KZnF_3$. The factor group is isomorphic with the point group O_h. The distribution of the fifteen degrees of freedom over the symmetry species of O_h is: $\Gamma = 4F_{1u} + F_{2u}$. The acoustical vibrations are classified by

F_{1u}. The calculated eigenvalues and eigenvectors are triply degenerate as is required by the proposed symmetry. The calculated eigenvalues, eigenvectors and potential energy distribution in the case of $KNiF_3$ agree with the calculation of Shimanouchi et al. if the same force constants are used. Note that in the present program the force constants in the case of the bending valence coordinates are set up with dimension mdyn Å/(rad)^2. The other force constants have the dimensions mdyn/Å. Although all calculated values agree with the value given by Shimanouchi et al. it is in some cases possible to calculate a slightly different force field of the perovskite structures, giving a smaller variance between the calculated and the observed frequencies [23].

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TEST RUN OUTPUT

```
$NAML
OPT     = F,
IFU     = F,
IFJ     = T,
IFP     = F,
IFB     = F,
PROID   = [illegible],
NOAT    = 5,
NOQ     = 5[illegible],
NOXS    = 15,
NOZ     = 30,
NOF     = 5,
NOIT    = 2,
$END
```

```
        NORMAL COORDINATE CALCULATION OF:
        PEROVSKITE STRUCTURE :KNIF3, ACCORDING TO I. NAKAGAWA, A. TSUCHIDA
        AND T. SHIMANOUCHI  (J. CHEM. PHYS.,47,982,1967).

ATOMIC WEIGHTS:
      58.690000   19.000000   19.000000   19.000000   39.100000

ELEMENTS OF B-MATRIX:
 1  3   -1.000000      1  6    1.000000      2  3    1.000000      2  6   -1.000000
 3  1   -1.000000      3  7    1.000000      4  1    1.000000      4  7   -1.000000
 5  2   -1.000000      5 11    1.000000      6  2    1.000000      6 11   -1.000000
 7  2     .498501      7  3     .498501      7  5    -.498501      7 12    -.498501
 8  2    -.498501      8  5     .498501      8  3     .498501      8 12    -.498501
 9  1     .498501      9 10    -.498501      9  2     .498501      9  8    -.498501
10  1     .498501     10 10    -.498501     10  2    -.498501     10  8     .498501
11  1    -.498501     11  2     .498501     11  8    -.498501     11 10     .498501
12  1    -.498501     12  2    -.498501     12  8     .498501     12 10     .498501
13  1     .498501     13  3     .498501     13  4    -.498501     13  9    -.498501
14  1    -.498501     14  3     .498501     14  4     .498501     14  9    -.498501
```

15	1	.498501	15	3	-.498501	15	4	-.498501	15	9	.498501
16	1	-.498501	16	3	-.498501	16	4	.498501	16	9	.498501
17	2	.498501	17	3	-.498501	17	5	-.498501	17	12	.498501
18	2	-.498501	18	3	-.498501	18	5	.498501	18	12	.498501
19	4	-.707107	19	6	.707107	19	7	.707107	19	9	-.707107
20	4	.707107	20	6	.707107	20	7	-.707107	20	9	-.707107
21	4	-.707107	21	6	-.707107	21	7	.707107	21	9	.707107
22	4	.707107	22	6	-.707107	22	7	-.707107	22	9	.707107
23	5	-.707107	23	6	.707107	23	11	.707107	23	12	-.707107
24	5	.707107	24	6	.707107	24	11	-.707107	24	12	-.707107
25	5	-.707107	25	6	-.707107	25	11	.707107	25	12	.707107
26	5	.707107	26	6	-.707107	26	11	-.707107	26	12	.707107
27	7	.707107	27	8	-.707107	27	10	-.707107	27	11	.707107
28	7	.707107	28	8	.707107	28	10	-.707107	28	11	-.707107
29	7	-.707107	29	8	-.707107	29	10	.707107	29	11	.707107
30	7	-.707107	30	8	.707107	30	10	.707107	30	11	-.707107
31	4	.707107	31	5	.707107	31	13	-.707107	31	14	-.707107
32	4	-.707107	32	5	.707107	32	13	.707107	32	14	-.707107
33	4	-.707107	33	5	-.707107	33	13	.707107	33	14	.707107
34	4	.707107	34	5	-.707107	34	13	-.707107	34	14	.707107
35	8	.707107	35	9	-.707107	35	14	-.707107	35	15	.707107
36	8	-.707107	36	9	-.707107	36	14	.707107	36	15	.707107
37	8	-.707107	37	9	.707107	37	14	.707107	37	15	-.707107
38	8	.707107	38	9	.707107	38	14	-.707107	38	15	-.707107
39	10	-.707107	39	12	-.707107	39	13	.707107	39	15	.707107
40	10	.707107	40	12	-.707107	40	13	-.707107	40	15	.707107
41	10	.707107	41	12	.707107	41	13	-.707107	41	15	-.707107
42	10	-.707107	42	12	.707107	42	13	.707107	42	15	-.707107
43	1	.577350	43	2	.577350	43	3	-.577350	43	13	-.577350
43	14	-.577350	43	15	.577350	44	1	-.577350	44	2	.577350
44	3	-.577350	44	13	.577350	44	14	-.577350	44	15	.577350
45	1	-.577350	45	2	-.577350	45	3	-.577350	45	13	.577350
45	14	.577350	45	15	.577350	46	1	.577350	46	2	-.577350
46	3	-.577350	46	13	-.577350	46	14	.577350	46	15	.577350
47	1	.577350	47	2	-.577350	47	3	.577350	47	13	-.577350
47	14	.577350	47	15	-.577350	48	13	.577350	48	14	.577350
48	15	-.577350	49	13	.577350	49	14	-.577350	49	15	-.577350
48	1	-.577350	48	2	-.577350	48	3	.577350	49	1	-.577350
49	2	.577350	49	3	.577350	50	1	.577350	50	2	.577350
50	3	.577350	50	13	-.577350	50	14	-.577350	50	15	-.577350
-5	-0	-0.000000	-0	-0	-0.000000	-0	-0	-0.000000	-0	-0	-0.000000

FORCE CONSTANTS:

.763000 .258000 .050000 .090000 .030000

ELEMENTS OF Z-MATRIX:

1	1	1	1.000000	2	2	1	1.000000	3	3	1	1.000000	4	4	1	1.000000
5	5	1	1.000000	6	6	1	1.000000	7	7	2	1.000000	8	8	2	1.000000
9	9	2	1.000000	10	10	2	1.000000	11	11	2	1.000000	12	12	2	1.000000
13	13	2	1.000000	14	14	2	1.000000	15	15	2	1.000000	16	16	2	1.000000
17	17	2	1.000000	18	18	2	1.000000	19	19	3	1.000000	20	20	3	1.000000
21	21	3	1.000000	22	22	3	1.000000	23	23	3	1.000000	24	24	3	1.000000
25	25	3	1.000000	26	26	3	1.000000	27	27	3	1.000000	28	28	3	1.000000
29	29	3	1.000000	30	30	3	1.000000	31	31	4	1.000000	32	32	4	1.000000
33	33	4	1.000000	34	34	4	1.000000	35	35	4	1.000000	36	36	4	1.000000
37	37	4	1.000000	38	38	4	1.000000	39	39	4	1.000000	40	40	4	1.000000
41	41	4	1.000000	42	42	4	1.000000	43	43	5	1.000000	44	44	5	1.000000
45	45	5	1.000000	46	46	5	1.000000	47	47	5	1.000000	48	48	5	1.000000
49	49	5	1.000000	50	50	5	1.000000								

DELTA= .005000 EPSILON= .001000 RHO= .316000

```
        OBSERVED FREQUENCIES
                446.0        -0.0        -0.0        255.0        -0.0        -0.0        -0.0        -0.0        -0.0        133.0
                 -0.0        -0.0        -0.0         -0.0        -0.0

WEIGHTED FACTORS P :
       .502724768E-05   0.              0.              .153787005E-04   0.              0.              0.
      0.                0.              .565323082E-04   0.              0.              0.              0.
      0.

FORCE CONSTANTS NUMBERS FOR VARIATION PROCESS:
              1   2   -0   -0   -0

        FREQUENCIES:
                445.3        445.3        445.3        252.0        252.0        252.0        219.0        219.0        219.0        144.3
                144.3        144.3          0.0          0.0          0.0
        S=      .007419
        ITER=  1     K=   1     DELTA=      .005000     S=          .0074183608

                                                                                                                  FC( 1)= .768000
        ITER=  1     K=   2     DELTA=      .005000     S=          .0076524214
        ITER=  1     K=   2     DELTA=     -.005000     S=          .0072247667

                                                                                                                  FC( 2)= .253000
        S0=      .007225
        REVISED FC
          .7680        .2530        .0500        .0900        .0300

        FREQUENCIES:
                446.6        446.6        446.6        250.8        250.8        250.8        218.0        218.0        218.0        144.1
                144.1        144.1          0.0          0.0          0.0
        S=      .007225
        ITER=  2     K=   1     DELTA=      .005000     S=          .0072409089
        ITER=  2     K=   1     DELTA=     -.005000     S=          .0072262391
        ITER=  2     K=   2     DELTA=      .005000     S=          .0074183599
        ITER=  2     K=   2     DELTA=     -.005000     S=          .0070721716

                                                                                                                  FC( 2)= .248000
        S0=      .007072
        REVISED FC
          .7680        .2480        .0500        .0900        .0300

FINAL VALUES OF FORCE CONSTANTS
                .7680        .2480        .0500        .0900        .0300

                 NO.     OBSERVED FREQ.    CALCULATED FREQ.   PTG ERROR
                  1            446.0             446.5             .1
                  2             -0.0             446.5             0.0
                  3             -0.0             446.5             0.0
                  4            255.0             249.7            -2.1
                  5             -0.0             249.7             0.0
                  6             -0.0             249.7             0.0
                  7             -0.0             216.9             0.0
                  8             -0.0             216.9             0.0
                  9             -0.0             216.9             0.0
                 10            133.0             143.8             8.1
                 11             -0.0             143.8             0.0
                 12             -0.0             143.8             0.0
                 13             -0.0               0.0             0.0
                 14             -0.0               0.0             0.0
                 15             -0.0               0.0             0.0
```

EIGENVECTORS

ROW= 1	0.000	-.490	0.000	-.355	0.000	0.000	-.000	0.000	0.000	0.000
	-.504	0.000	0.000	.616	0.000					
ROW= 2	-.490	0.000	0.000	0.000	0.000	-.355	0.000	0.000	-.000	-.504
	0.000	0.000	0.000	0.000	.616					
ROW= 3	0.000	0.000	-.490	0.000	-.355	0.000	0.000	-.000	0.000	0.000
	0.000	-.504	.616	0.000	0.000					
ROW= 4	0.000	-.012	0.000	.614	0.000	0.000	-.707	0.000	0.000	0.000
	.007	0.000	0.000	.350	0.000					
ROW= 5	-.011	0.000	0.000	0.000	0.000	.614	0.000	0.000	-.707	.007
	0.000	0.000	0.000	0.000	.350					
ROW= 6	0.000	0.000	.872	0.000	-.180	0.000	0.000	-.000	0.000	0.000
	0.000	-.292	.350	0.000	0.000					
ROW= 7	0.000	.871	0.000	-.180	0.000	0.000	-.000	0.000	0.000	0.000
	-.292	0.000	0.000	.351	0.000					
ROW= 8	-.011	0.000	0.000	0.000	0.000	.614	0.000	0.000	.707	.007
	0.000	0.000	0.000	0.000	.351					
ROW= 9	0.000	0.000	-.011	0.000	.614	0.000	0.000	-.707	0.000	0.000
	0.000	.007	.350	0.000	0.000					
ROW= 10	0.000	-.012	0.000	.614	0.000	0.000	.707	0.000	0.000	0.000
	.007	0.000	0.000	.351	0.000					
ROW= 11	.871	0.000	0.000	0.000	0.000	-.180	0.000	0.000	-.000	-.292
	0.000	0.000	0.000	0.000	.350					
ROW= 12	0.000	0.000	-.011	0.000	.614	0.000	0.000	.707	0.000	0.000
	0.000	.007	.351	0.000	0.000					
ROW= 13	0.000	.009	0.000	-.295	0.000	0.000	-.000	0.000	0.000	0.000
	.812	0.000	0.000	.503	0.000					
ROW= 14	.009	0.000	0.000	0.000	0.000	-.295	0.000	0.000	-.000	.812
	0.000	0.000	0.000	0.000	.503					
ROW= 15	0.000	0.000	.010	0.000	-.295	0.000	0.000	-.000	0.000	0.000
	0.000	.812	.503	0.000	0.000					

J-MATRIX: (COL.NO. IS NO.OF FORCE CONSTANTS, ROW NO. IS NO.OF FREQUENCY)

ROW= 1	.139	.007	.164	.000	.011
ROW= 2	.139	.007	.164	.000	.011
ROW= 3	.139	.007	.164	.000	.011
ROW= 4	.000	.070	.133	.142	.000
ROW= 5	.000	.070	.133	.142	.000
ROW= 6	.000	.070	.133	.142	.000
ROW= 7	.000	.052	.105	.105	.000
ROW= 8	.000	.052	.105	.105	.000
ROW= 9	.000	.052	.105	.105	.000
ROW= 10	.000	.009	.019	.066	.102
ROW= 11	.000	.009	.019	.066	.102
ROW= 12	.000	.009	.019	.066	.102
ROW= 13	.000	.000	.000	.000	.000
ROW= 14	.000	.000	.000	.000	.000
ROW= 15	.000	.000	.000	.000	.000

POTENTIAL ENERGY DISTRIBUTION
COL.NO. IS NO. OF FORCE CONSTANT AND ROW IS FEQ. NO.

ROW= 1	.911	.016	.070	.000	.003
ROW= 2	.911	.016	.070	.000	.003
ROW= 3	.911	.016	.070	.000	.003
ROW= 4	.001	.471	.181	.347	.000
ROW= 5	.001	.471	.181	.347	.000
ROW= 6	.001	.471	.181	.347	.000
ROW= 7	.000	.468	.190	.342	.000
ROW= 8	.000	.468	.190	.342	.000
ROW= 9	.000	.468	.190	.342	.000
ROW= 10	.000	.184	.077	.487	.252
ROW= 11	.000	.184	.077	.487	.252
ROW= 12	.000	.184	.077	.487	.252

LX MATRIX (CARTESIAN)

ROW= 1									
0.000	-.064	0.000	-.046	0.000	0.000	-.000	0.000	0.000	0.000
-.066	0.000	0.000	.080	0.000					
ROW= 2									
-.064	0.000	0.000	0.000	0.000	-.046	0.000	0.000	-.000	-.066
0.000	0.000	0.000	0.000	.080					
ROW= 3									
0.000	0.000	-.064	0.000	-.046	0.000	0.000	-.000	0.000	0.000
0.000	-.066	.080	0.000	0.000					
ROW= 4									
0.000	-.003	0.000	.141	0.000	0.000	-.162	0.000	0.000	0.000
.002	0.000	0.000	.080	0.000					
ROW= 5									
-.003	0.000	0.000	0.000	0.000	.141	0.000	0.000	-.162	.002
0.000	0.000	0.000	0.000	.080					
ROW= 6									
0.000	0.000	.200	0.000	-.041	0.000	0.000	-.000	0.000	0.000
0.000	-.067	.080	0.000	0.000					
ROW= 7									
0.000	.200	0.000	-.041	0.000	0.000	-.000	0.000	0.000	0.000
-.067	0.000	0.000	.080	0.000					
ROW= 8									
-.003	0.000	0.000	0.000	0.000	.141	0.000	0.000	.162	.002
0.000	0.000	0.000	0.000	.080					
ROW= 9									
0.000	0.000	-.003	0.000	.141	0.000	0.000	-.162	0.000	0.000
0.000	.002	.080	0.000	0.000					
ROW= 10									
0.000	-.003	0.000	.141	0.000	0.000	.162	0.000	0.000	0.000
.002	0.000	0.000	.080	0.000					
ROW= 11									
.200	0.000	0.000	0.000	0.000	-.041	0.000	0.000	-.000	-.067
0.000	0.000	0.000	0.000	.080					
ROW= 12									
0.000	0.000	-.003	0.000	.141	0.000	0.000	.162	0.000	0.000
0.000	.002	.080	0.000	0.000					
ROW= 13									
0.000	.001	0.000	-.047	0.000	0.000	-.000	0.000	0.000	0.000
.130	0.000	0.000	.080	0.000					
ROW= 14									
.001	0.000	0.000	0.000	0.000	-.047	0.000	0.000	-.000	.130
0.000	0.000	0.000	0.000	.080					
ROW= 15									
0.000	0.000	.002	0.000	-.047	0.000	0.000	-.000	0.000	0.000
0.000	.130	.080	0.000	0.000					